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THE KINETICS OF MECHANISM FOR THE  
SUBSTITUTION OF BIPHENYLOXIDE FOR CHLORIDE ON  
HEXAPHENYLDICHLOROTETRAPHOSPHONITRILE

by

John Hay McCorry



# United States Naval Postgraduate School



## THESIS

THE KINETICS AND MECHANISM FOR THE SUBSTITUTION  
OF  
BIPHENYLOXIDE FOR CHLORIDE  
ON  
HEXAPHENYLDICHLOROTETRAPHOSPHONITRILE

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John Hay McCorry

June 1969

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The Kinetics and Mechanism for the Substitution of Biphenyloxide  
for Chloride on Hexaphenyldichlorotetraphosponitrile

by

John Hay McCorry  
Lieutenant Commander, United States Navy  
B.S., University of Notre Dame, 1958

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ABSTRACT

In this research a study of the kinetics and mechanism of the biphenyloxy substitution for chloride on the hexaphenyldichlorotetra-phosphonitrile molecule was conducted. The reaction was studied in sealed, evacuated ampoules at 210°C and in an evacuated gas pressure measuring system at temperatures of 185°C and 195°C.

Two isomers of the expected disubstituted product were isolated by fractional recrystallization from acetonitrile. The isomers had melting points of 204°C and 174°C.

The gas pressure studies provided extent of reaction versus time curves. An analog computer was used to simulate the reaction and the rates obtained were used to determine the Entropy of activation as  $-42.5 \pm 10.0 \text{ cal mole}^{-1} \text{ degree K}^{-1}$  and Enthalpy of activation as  $13.6 \pm 10.0 \text{ Kcal mole}^{-1}$  for the first substitution.

A mechanism consistent with these values is proposed and discussed.

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## I. INTRODUCTION

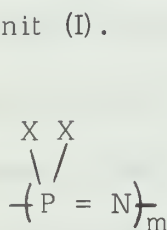
For the past fifteen years, numerous studies have been undertaken to improve the quality of phosphonitrile organic-inorganic polymers. The work described in this report was undertaken with the hope of determining the reaction mechanism for the polymerization of hexaphenyldichlorotetraphosponitrile and bisphenol. It seemed likely that this could offer the key for improving such polymers.

Since the bisphenol caused ring linkage of varying degree thereby making isolation and characterization of a product virtually impossible, this study was conducted using p-hydroxybiphenyl as the nucleophile. This would prevent polymerization from occurring and thus allow isolation and characterization of the product. This nucleophile was chosen because it closely resembles bisphenol sterically as well as in acidity.

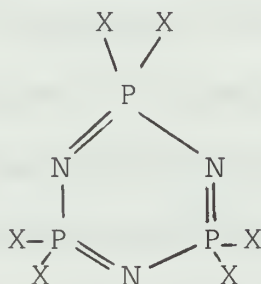
Isolation of this reaction product, the twice substituted tetramer, was reported in (1).

## II. HISTORICAL

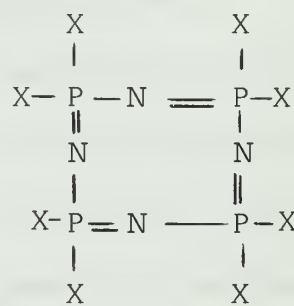
In 1834, LIEBIG announced the discovery of trimeric chlorophosphonitrile (2). Little was done with this discovery until the latter part of the nineteenth century, when an American chemist H. N. STOKES prepared an isolated series of chlorophosphonitrile polymers  $(NPCl_2)_n$ , where  $n = 3-7$  (3, 4, 5, 6, 7, 8, 9). The important structural characteristic of this series is the unsaturated repeating unit (I).



(I)



(II)

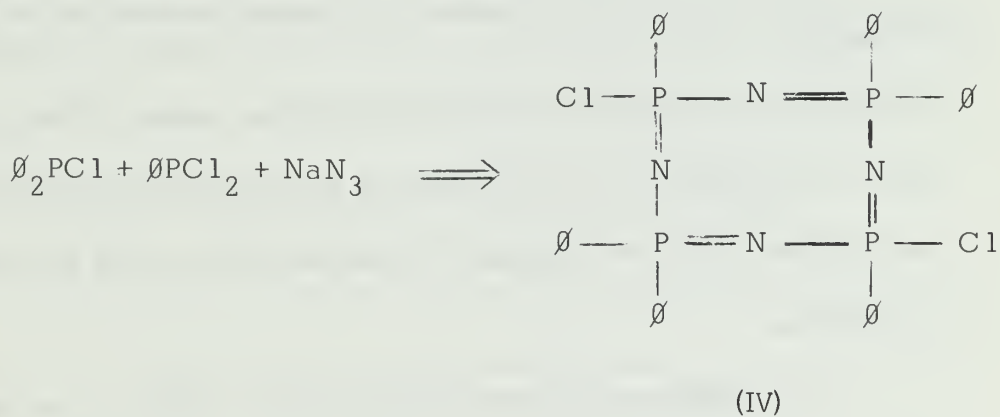


(III)

STOKES (9) proposed a planar cyclic structure for hexachlorotriphosphonitrile (II). This structure was confirmed by electron diffraction measurements of (II) by BROCKWAY and BRIGHT (10) and SCHOMAKER (11). Structural determination from x-ray diffraction patterns by KETLAAR and deVRIES (12, 13) showed octachlorotetraphosphonitrile (III) to be a puckered, eight-membered ring containing alternate nitrogen and phosphorous atoms, with two chlorine atoms attached to each phosphorous.

Again, little was done in the study of phosphonitriles until the nineteen fifties when a great need developed for a flame resistant polymer for high temperature use. Many hoped to find the answer to this problem in a phosphonitrile inorganic polymer. The available reviews of these efforts include PADDOCK (14), SHAW et al (15), SCHMULBACH (16) and HABER (17). Although all are excellent, HABER's work is particularly germane to this article, because it was his associates at the NAVAL ORDNANCE LABORATORY, CORONA, CALIF., who carried out most of the work leading to the problem reported here.

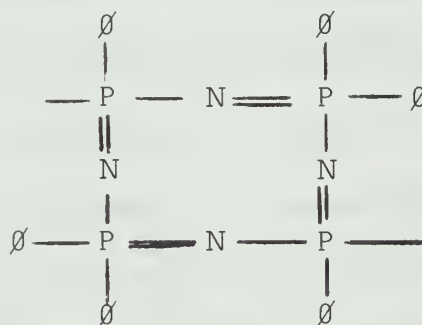
The group at CORONA developed numerous synthetic procedures for placing different inorganic and organic substituents where desired on a wide variety of cyclic and linear phosphonitriles. Of specific interest was HERRING and DOUGLAS' (18) syntheses of hexaphenyldichlorotetra-phosphonitrile compound (IV) in reasonable yields by the reaction:



This compound has been shown to exist in both trans (mp 303-304°C) and cis (mp 189-190°C) configurations.

The work at CORONA finally evolved into a search for a satisfactory ring linkage of the above mentioned dichlorotetraphosphonitrile, to form organic-inorganic polymers.

The notation hereafter used in discussing the dichlorohexaphenyltetraphosphonitrile will be that adopted by the CORONA group (18), namely the hexaphenyltetraphosphonitrile structure (V) is hereafter abbreviated as  $\square$  or  $\diamond$  and in the case of cyclic monomers as  $\underline{T}$  only.



(V)

Among the studies reported in (1), were the thermal isomerization of the trans  $\text{TCl}_2$  to cis  $\text{TCl}_2$  at  $265^\circ\text{C}$  and chemical isomerization by refluxing thionylchloride with the hydrolysis product  $\text{T}(\text{OH})_2$  in chloroform. Of interest is the fact that use of phosphorouspentachloride as the chlorinating agent produces no isomerization under the same conditions.

Diaminohexaphenyltetraphosphonitrile,  $\text{T}(\text{NH}_2)_2$ , was prepared by bubbling ammonia gas into a chloroform suspension of  $\text{TCl}_2$ . Polymerization attempts on  $\text{T}(\text{NH}_2)_2$  produced the expected structure  $\left( \text{---} \square \text{---} \text{NH} \right)_x$ .

(However x could not be forced above 2.) In other diamine studies it was found that HCl cleaved dimethylamino groups from the T ring with nearly quantitative regeneration of  $\text{TC1}_2$ .

Additional polymerization attempts were made using diols. The most common experimental technique was the use of the diol in the melt as solvent. The reactions were always run at temperatures above  $210^\circ\text{C}$ , under vacuum and with continuous withdrawal of any gases evolved. Most of the reactions were run with either resorcinol or bisphenol as the ring linking agent.

Polymers which had fractions with molecular weights as high as 269,000 were obtained. The softening range of these polymers was  $180\text{--}220^\circ\text{C}$ . In general, they were hard, glossy, brittle, amber solids at room temperature.

In the bisphenol- $\text{TC1}_2$  studies, all attempts to increase the quality of the polymer product by varying the reaction conditions failed.

### III. EXPERIMENTAL

#### A. PURIFICATION OF STARTING MATERIALS

##### 1. Twice Recrystallized Tetramer

Three gms of once recrystallized  $\text{TC1}_2$  per hundred ml of chlorobenzene were refluxed for twelve hours. The solution was allowed to cool to room temperature by slowly lowering the heating mantle over a period of two hours. After twelve hours, the crystalized  $\text{TC1}_2$  was dried under vacuum (mp  $299-301^\circ\text{C}$ ).

##### 2. Once Recrystallized Tetramer

Approximately three gms of commercial  $\text{TC1}_2$  per hundred ml of chlorobenzene were set to boiling until all  $\text{TC1}_2$  dissolved in chlorobenzene. The solution was then allowed to cool for twenty-four hours.  $\text{TC1}_2$  crystalized out as a coating on the beaker. The chlorobenzene was decanted and the  $\text{TC1}_2$  scraped into a weighing bottle and set to drying under vacuum (mp  $292-295^\circ\text{C}$ ).

##### 3. p-Hydroxybiphenyl

A solution of 50% water and 50% EtOH was set to boiling and p-hydroxybiphenyl was added until it would no longer go into solution. At this point, more solvent mixture was added until all the p-hydroxybiphenyl was in solution. After standing for twenty-four hours, the solvent was decanted and the wet p-hydroxybiphenyl was set to drying under vacuum (mp  $163.5-164.5^\circ\text{C}$ ).

## B. SEALED AMPUOLE TESTS

In an approximate ratio of four moles of p-hydroxybiphenyl to one mole of  $\text{TCI}_2$ , the starting materials were weighed separately into a five-inch test tube. The material was carefully placed in the test tube to insure that none of the material was adhering to the upper portion of it. The test tubes were then sealed under vacuum. No measurement of the actual pressure was made on any of these test tubes. It is estimated, however, that the pressure varied from twenty mm to two hundred mm of Hg.

For a given test, all the sealed tubes were simultaneously immersed into an electrically controlled oil bath at  $210^\circ\text{C}$ . At varying time intervals, the tubes were removed from the oil bath and washed with benzene to remove the oil.

The test tubes were then placed in four hundred ml beakers and covered with three hundred ml of distilled water. The tubes were then broken, allowing the water into the tube to absorb any  $\text{HCl}$  produced by the reaction. Using a pHmeter, the resulting solution was then titrated with  $\text{NaOH}$  solution which had been standardized against KHP.

After the water had evaporated from the above beakers, the material remaining in the broken test tubes was washed with boiling benzene into 25 ml erlenmeyer flasks. The benzene was evaporated off. The remaining solid was washed with cold acetonitrile and allowed to stand. After approximately twelve hours, the liquid portion was decanted into another flask. The solid remaining in the original flask was put into

solution with a minimum of boiling acetonitrile. After approximately twelve hours, the liquid was once again decanted into a third flask and the crystals which were left behind were dried under vacuum. These crystals were weighed and mp determinations made. All of this material was later recrystallized to obtain a sample which had an mp of 201-203°C; (ir 3145, 3072, 3056, 3033, 3012, 2995, 2922, 2851, 1958, 1891, 1601, 1512, 1481, 1449, 1436, 1311, 1290, 1202, 1164d, 1114d, 1067, 1036, 1024, 1017, 1008, 996, 891d, 841, 792, 763, 745, 718, 705, 691, 660d, 638, 612, 573, 553, 531, 521, 511, 450  $\text{cm}^{-1}$ ).

Analysis (for  $\text{T}(\text{O}\emptyset\emptyset)_2$ )

	P	N	C	H	Cl
Calc'd	12.68	5.72	73.5	4.9	0.0
Found	12.4	5.8	73.3	4.9	0.08

The second solution from which the above product was obtained, was allowed to sit for approximately one week, after which, in a number of cases, additional crystals were found to have formed. These crystals were dried under vacuum and weighed. These crystals were found to have a melting point of 172-173°C; (ir 3074, 3057, 3029, 3009, 2991, 1953, 1887, 1601, 1509, 1480, 1448, 1433, 1311, 1290, 1201, 1192, 1171, 1161, 1114, 1063, 1035, 1023, 1015, 1006, 994, 887d, 839, 793, 772, 758, 741, 713, 705, 687, 659, 632, 615, 572, 554, 542, 533, 509, 451  $\text{cm}^{-1}$ ).

Analysis (for  $\text{T}(\text{O}\emptyset\emptyset)_2$ )

	P	N	C	H	Cl
Calc'd	12.68	5.72	73.5	4.9	0.0
Found	12.5	5.9	73.6	5.0	0.11

The two materials described above will be referred to as high melter (mp 204°C) and low melter (mp 174°C)  $T(000)_2$ .

#### C. SEALED SYSTEM WITH HCl ABSORBER

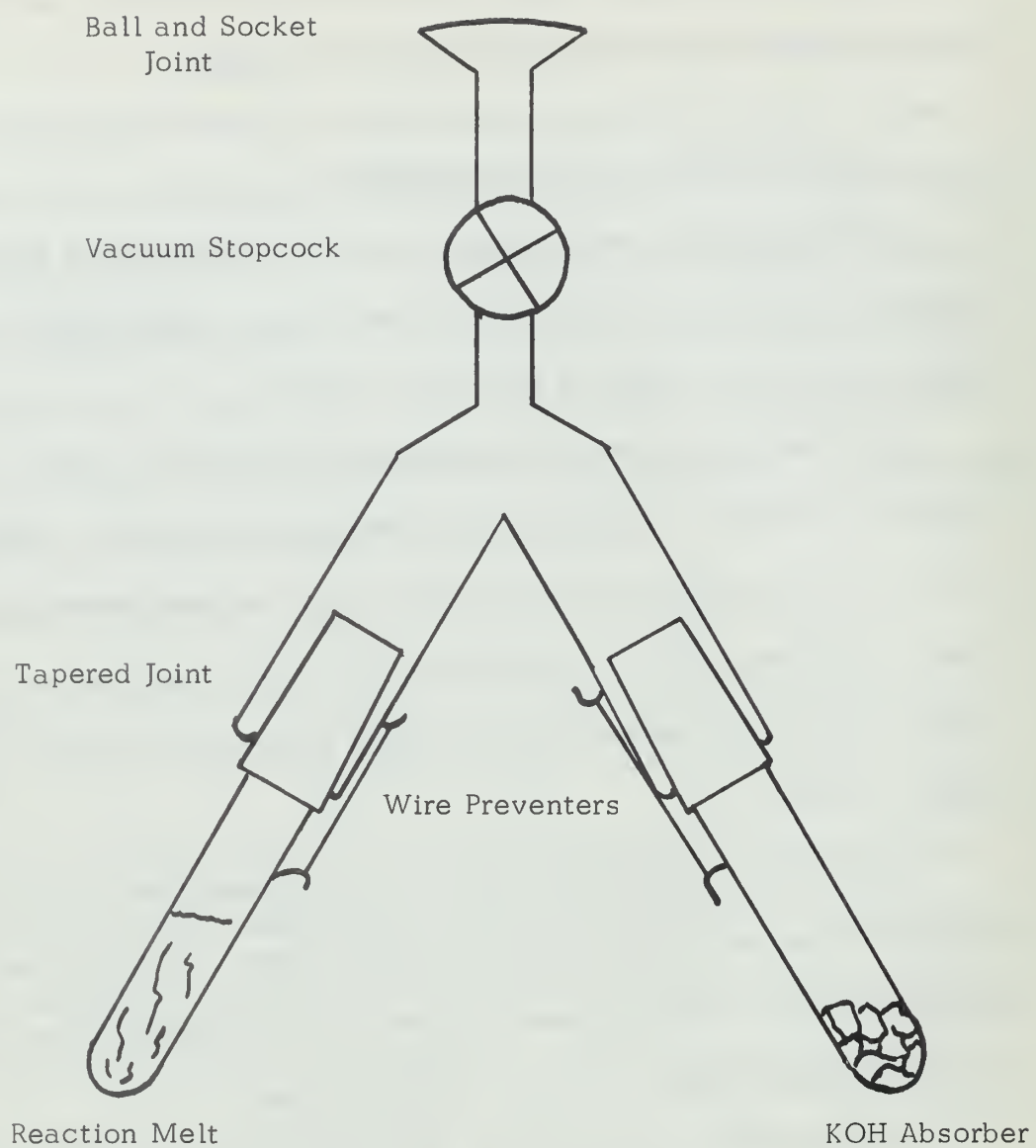
Reaction vessels were manufactured which would allow for KOH to be used as an HCl absorber without being in the reaction melt. A simple line diagram of the apparatus is shown in Figure 1.

For these tests, the p-hydroxybiphenyl and the  $TC1_2$  were separately weighed into one of the tapered joint test tubes. Approximately 0.5 gms of KOH were then added to the second tapered joint test tube. The tubes were then smeared with silicone grease and the joints secured with wire to prevent losing the test tubes in the oil bath in the event of a failure.

The rig was then placed under vacuum (approximately 2 mm Hg) and the KOH heated to drive off any possible water. After sealing and removing from the vacuum system, the rig was immersed into the oil bath at various temperatures for various lengths of time.

At the end of the desired time, the rig was removed from the oil bath and plunged into an ice bath to quench the reaction. After the material in the rig solidified, the adherent oil was removed with benzene and the rig opened to the air. The test tube containing the KOH was removed and weighed to determine if there had been a significant change in weight. In all cases, there was less than 0.1 gms change in weight.

The test tube containing the reaction material was then washed with the boiling benzene and transferred to a fifty ml erlenmeyer flask.



Reaction Vessel for 210°C KOH Absorber Runs

Figure 1

In all cases, there was a varying amount of material which did not go into solution in the boiling benzene; this material had an mp of 275-285°C and is considered to be contaminated  $\text{TC1}_2$ . The benzene was then evaporated from the fifty ml flask and then dried under vacuum. The flasks were weighed. In general, the flasks were found to contain between 85-95 percent of the mass of the original materials. This material was washed with cold acetonitrile and allowed to stand for approximately six hours. The cold acetonitrile solution was decanted to another flask and the remaining insoluble material was put into solution with a minimum amount of boiling acetonitrile.

The boiling solution was set aside for twenty-four hours to allow for recrystallization, after which the liquid was decanted to another flask. After allowing this second flask to evaporate to the atmosphere for about twenty-four hours, additional crystals were formed. These crystals, as well as those first recrystallized, were dried in vacuum and found to be mostly high melting  $\text{T(000)}_2$ . However, in some cases a small quantity of the low melter could be detected in the second recrystallization.

The liquid which was decanted from the first acetonitrile cold wash was found to recrystallize some material on standing to the air, which could be purified to both high and low melting  $\text{T(000)}_2$ . In addition, the remaining material could be separated by sublimation at 130°C into pure p-hydroxybiphenyl and a sticky brownish material, mp 52-58°C; (ir 3074, 3058, 3032, 2926, 2855, 1602, 1512, 1482, 1435, 1310,

1285, 1204, 1200, 1175, 1163, 1115d, 1093, 1035, 1023, 1015, 1005, 994, 900, 841, 800, 775, 761, 744, 713, 691, 642, 612, 572, 552, 530, 510, 450  $\text{cm}^{-1}$ ).

Analysis (for  $\text{T}(\text{O}\text{O})_2$ )

	P	N	C	H	Cl
Calc'd.	12.68	5.72	73.5	4.9	0.0
Found	11.25	5.02	73.34	4.99	0.29

#### D. DTA STUDIES

##### 1. Isomerization of $\text{TC1}_2$

A sample of once recrystallized  $\text{TC1}_2$  was heated in the DTA to its melting point and cooled. When run a second time, there were two melting points noted, one at  $61^\circ\text{C}$  and one at  $285^\circ\text{C}$ . Upon a second cooling and reheating, the amount of material melting at the lower mp was found to be greater than on the previous run. As would be expected, there was less high melter also. On the next cycle, it was found that all the material melted at  $60^\circ\text{C}$ .

##### 2. p-Hydroxybiphenyl $\text{TC1}_2$ Reaction Studies

An arbitrary amount of once recrystallized  $\text{TC1}_2$  mixed with p-hydroxybiphenyl in a one-to-four molar ratio was placed in the DTA. The DTA was then heated at  $20^\circ\text{C}$  per minute to  $210^\circ\text{C}$ . At  $165^\circ\text{C}$ , the  $\text{O}\text{O}\text{H}$  was found to begin melting. At about  $175^\circ\text{C}$ , it was apparent that some exothermic reaction was taking place and that some material was leaving the sample. This differed markedly from a pure  $\text{O}\text{O}\text{H}$  run, in which the material melted  $165^\circ\text{C}$ , but there was no sign of significant sublimation until at least  $245^\circ\text{C}$ .

## E. GAS PRESSURE STUDIES

These studies were undertaken utilizing an existing vacuum system and mounted manometer. A reaction vessel was constructed which could be attached to the existing system by a ball and socket joint. The reaction vessel's base was specifically made large enough to accommodate a half-inch stirrer.

For a specific run, approximately 2 gms of each of the starting materials were carefully weighed into the reaction vessel. The reaction vessel was then installed on the vacuum system and evacuated to 10 microns pressure. After the reaction vessel was satisfactorily evacuated, an oil bath mounted on an electric stirrer was raised quickly to engulf the reaction chamber. This oil bath was controlled by manual adjustments to a variac. The temperature was controlled to  $\pm 0.5^{\circ}\text{C}$ . The changes in the pressure of the system were recorded versus time. At the beginning of the reaction, readings were taken every fifteen seconds, as the reaction passed the ten-minute mark, the intervals between readings were changed to thirty seconds. At the twenty-minute point, the interval for readings was lengthened to one minute. Readings were continued until the system reached equilibrium.

Such runs were made twice at  $185^{\circ}\text{C}$  and three times at  $195^{\circ}\text{C}$ . On two of the runs after equilibrium was reached, the temperature was raised in steps to  $195^{\circ}\text{C}$ ,  $205^{\circ}\text{C}$  and  $210^{\circ}\text{C}$ . At each of these temperatures, a new equilibrium was established. The temperature was then lowered in steps to  $205^{\circ}\text{C}$ ,  $195^{\circ}\text{C}$ ,  $185^{\circ}\text{C}$  and  $175^{\circ}\text{C}$ . At each temperature, equilibrium was established again.

When the reaction vessel was removed from the vacuum system, it was found that some of the p-hydroxybiphenyl had sublimed to a point in the neck of the reaction vessel just above what had been the level of hot oil. The amount of material which had sublimed was not determined. It was noted that the sublimed material occupied a volume equal to three quarters of a cubic centimeter. The sublimation appeared to be complete within ten minutes of the start of reaction. No attempt was made to include this loss of p-hydroxybiphenyl in the later calculations. It has been assumed that the error would be relatively constant between runs.

In addition, after one of the runs, the gas in the system was collected and analyzed in a mass spectrometer. This analysis showed a relatively high percentage of water equal to one-third the total gas. This high percentage is attributed to the fact that all the moisture which was present in the collecting container was not completely removed before collecting the gas. Assuming this to be true, it was found that 95% of the gas was HCl. The remaining peaks could generally be attributed to the solvents which had earlier been used to purify the starting materials.

#### IV. RESULTS

The data for the first fifteen minutes of each gas run were plotted and are shown as Figures 2 through 6. In addition, the data was graphed to determine whether the reaction was first or second order. These graphs indicated that the reaction was second order.

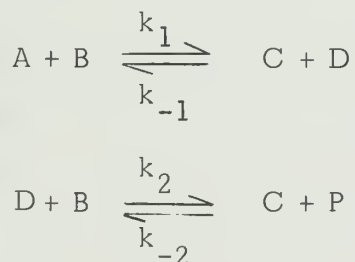
Based on this and the assumption that the reaction goes through an intermediate of the form  $\text{ClT0}\emptyset\emptyset$ , an attempt was made to fit the output of an analog computer to the graphs of pressure versus time, Figures 2 through 6. The analog computer was programmed to solve the three differential equations

$$\frac{d(C)}{dt} = k_1 (A)(B) + k_2 (D)(B) - k_{-1} (C)(D) - k_{-2} (C)(P)$$

$$\frac{d(D)}{dt} = k_1 (A)(B) + k_{-2} (C)(P) - k_{-1} (C)(D) - k_2 (D)(B)$$

$$\frac{d(P)}{dt} = k_2 (D)(B) - k_{-2} (C)(P)$$

corresponding to a reaction formulated as



where,  $A = \text{TC1}_2$

$B = \text{H0}\emptyset\emptyset$

$C = \text{HCl}$

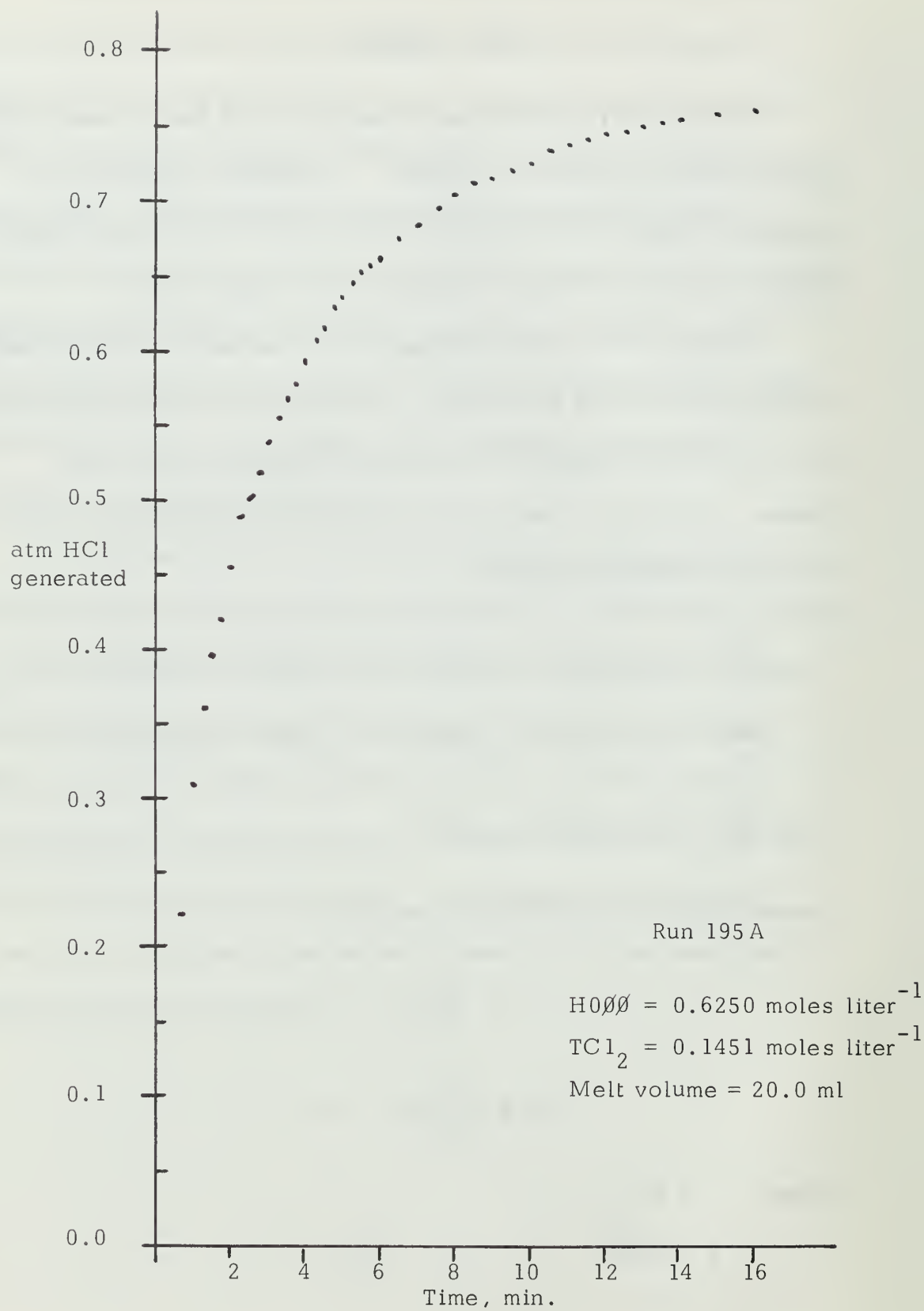


Figure 2

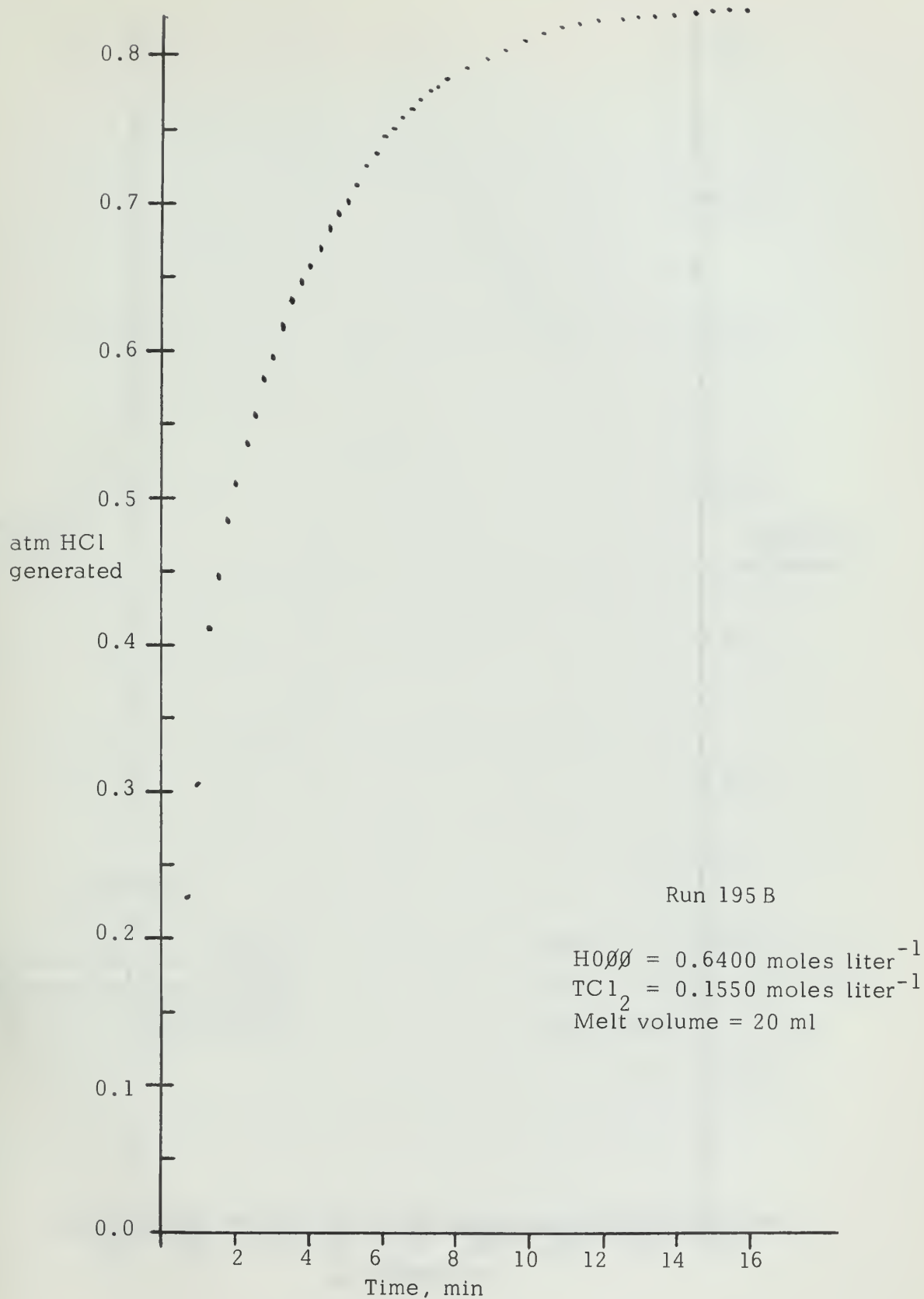


Figure 3

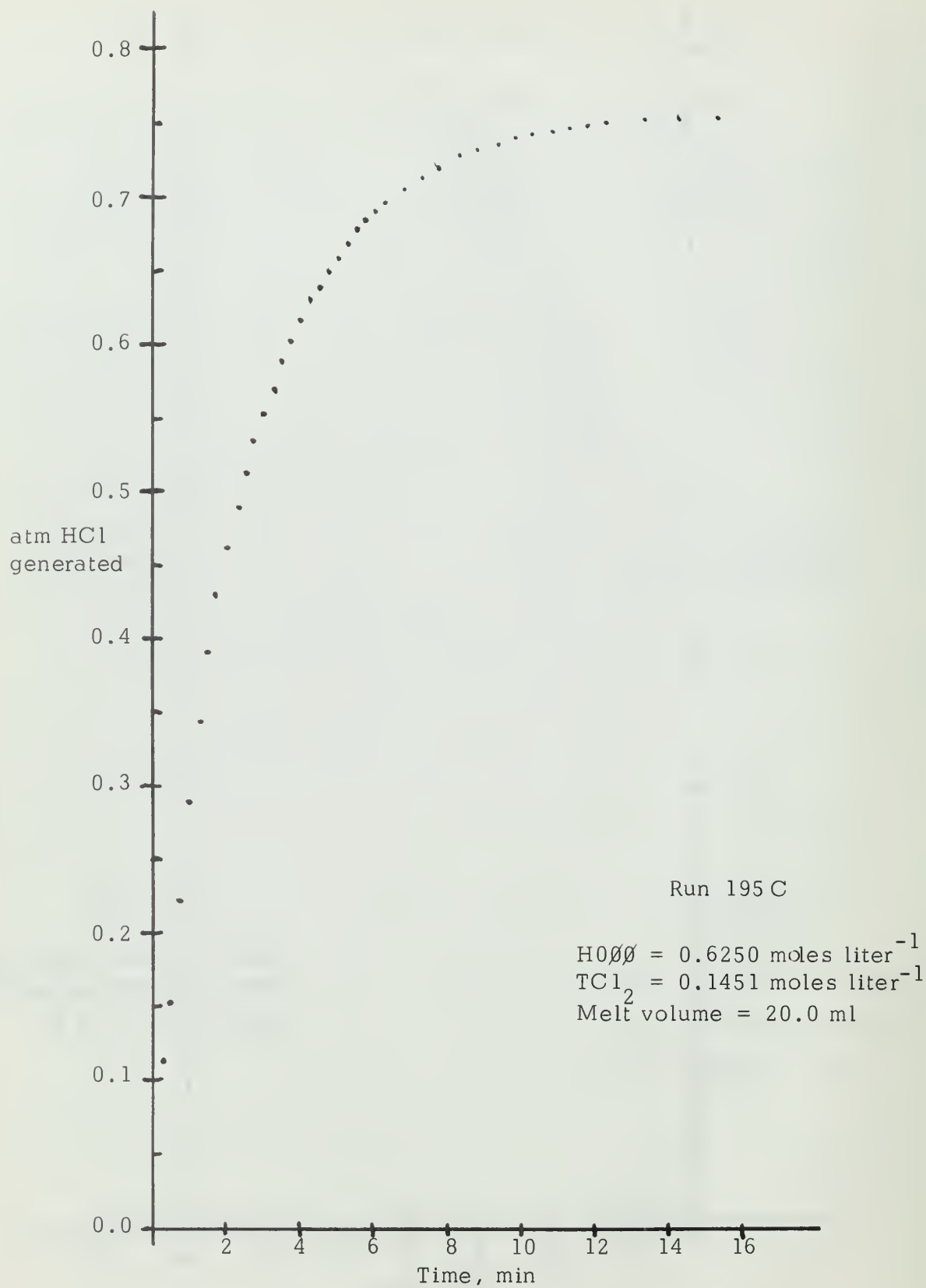


Figure 4

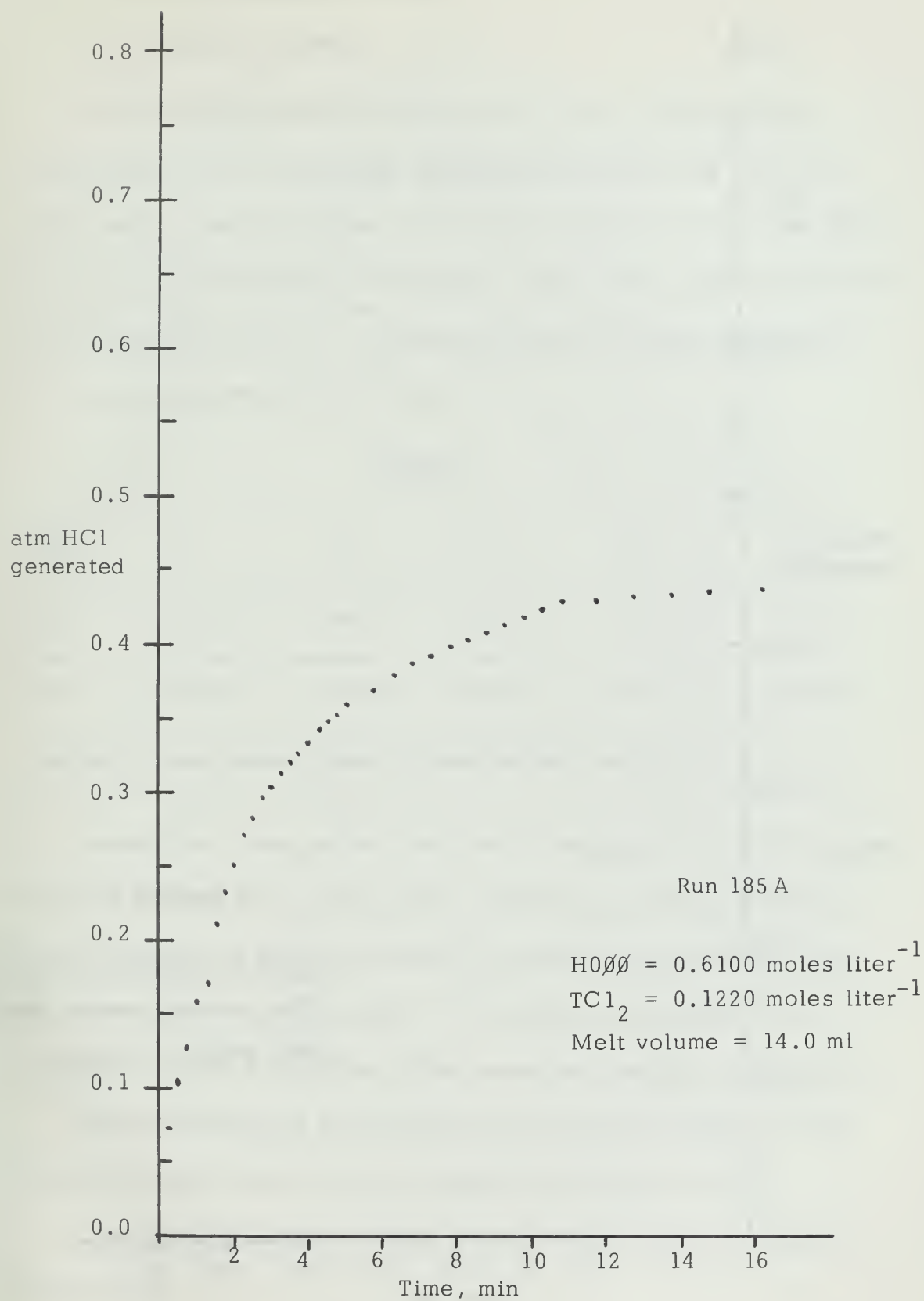


Figure 5

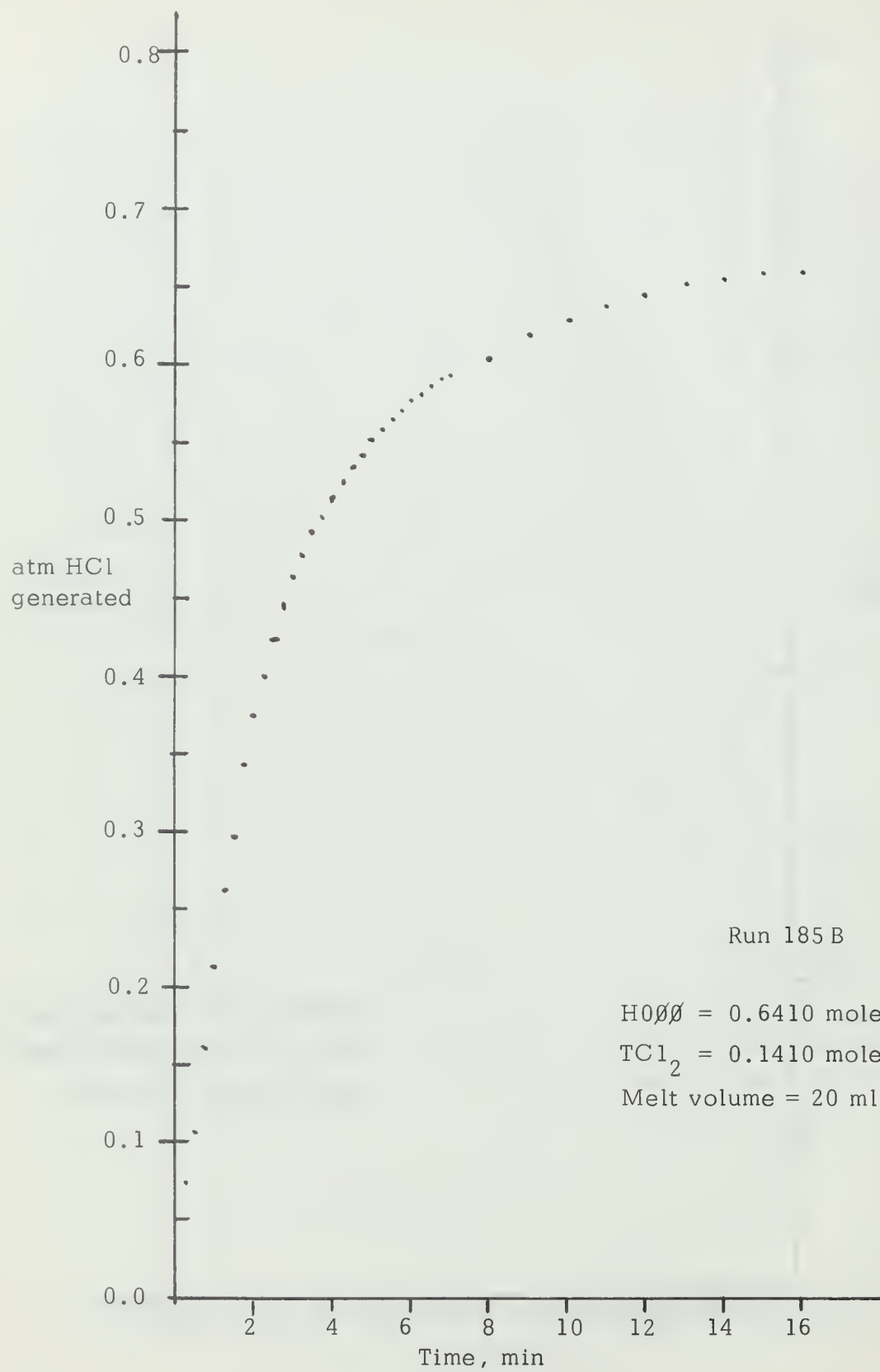


Figure 6

D = intermediate Cl T 000

P = product T(000)<sub>2</sub>

A virtual reproduction was obtained for runs 195C and 185B.

All the other curves agreed with the plotted data during the first 50% of the reaction and also during the last five minutes of the plotted data. The only variance occurred at the bend in these curves and the deviation never exceeded 0.05 atm. The rate constants have been averaged for the runs and are presented in Table I.

TABLE I

Temp.	$k_1$	$k_2$	$k_{-1}$	$k_{-2}$	$k_{eq}$
195	$1.82 \pm .15$	$.784 \pm .1$	$.633 \pm .1$	$1.27 \pm .1$	1.782
185	$1.29 \pm .15$	$.379 \pm .1$	$.633 \pm .1$	$1.27 \pm .1$	.638
Degrees in Centigrade, Rates in liters moles <sup>-1</sup> seconds <sup>-1</sup>					

In addition, these values were used to extrapolate to a set of rates for 205°C. These values were used in the analog computer with the initial conditions of the run for which the temperature had been raised and lowered through various steps. The output at equilibrium times compared to within 1.5% of the actual pressures observed at equilibrium.

The percentages of HCl titrated and the percent T(000)<sub>2</sub> isolated during the sealed vessel runs are reported in Tables II and III.

The rates of reaction in Table I were used in the thermodynamic relationships,

TABLE II

210° SEALED AMPUOLE RUNS AVERAGE OF TWO RUNS

Time in min.	Percent available HCl determined by titration	Percent T(000) <sub>2</sub> isolated
1.45	0.0	0.0
10.00	28.8	45.0
20.00	31.0	48.0
30.00	30.0	38.0
40.00	23.0	34.0
60.00	15.0	65.0

TABLE III

KOH ABSORBER RUNS AT 210°C

Time in min.	Percent T(000) <sub>2</sub> isolated
4.0	31.1
8.0	62.2
# 10.0	60.0
15.5	64.7
20.0	50.1

# average value for two runs.

$$\Delta F^\ddagger = -RT \ln \left( \frac{k_r}{kT} \right)$$

$$\Delta H^\ddagger = -R \left( \frac{d(\ln k_r)}{d(1/T)} + T \right)$$

$$\Delta S^\ddagger = R \left( T \frac{d(\ln k_r)}{dT} + \ln \frac{k_r}{kT} - 1 \right)$$

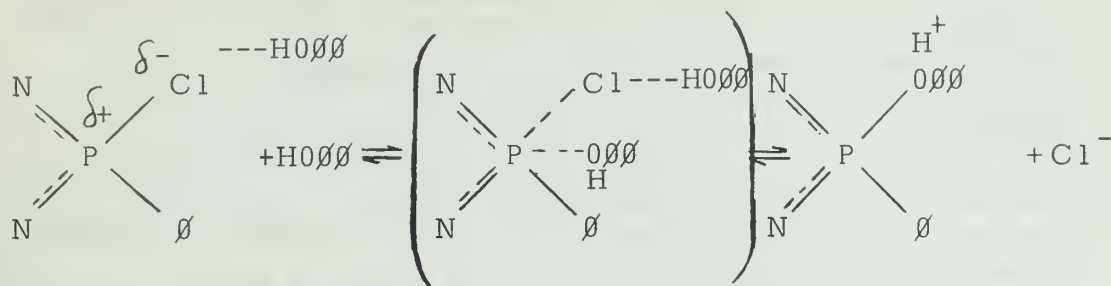
to obtain an Entropy of activation of  $-42.5 \pm 10.0 \text{ cal mole}^{-1} \text{ degree K}^{-1}$  and Heat of activation of  $13.6 \pm 10.0 \text{ K cal mole}^{-1}$  for the first substitution. The  $H$  of the complete reaction is  $43.5 \pm 10.0 \text{ K cal mole}^{-1}$ .

## V. DISCUSSION

### A. SEALED AMPUOLE DATA

Although the values in Tables II and III are suspect as to how accurately they portray the exact reaction concentrations, certain valuable information was obtained from the closed ampoule runs. First, of course, the fact that commercial analysis shows without a doubt that both chlorides have been replaced, this is significant to the interpretation of the gas pressure studies. Secondly, the data was significant in that it established the order of magnitude of the rate of reaction. Prior to this, based on the long reaction times reported in reference 1, for the reaction involving bisphenol, a slow reaction rate was expected. Third, the isolation of the product in two isomers raises reasonable doubt as to the necessity of purifying the high melting isomer for the polymerization studies. The work reported here does not resolve this question since the purest starting material used in any of the reactions still had a two-degree spread at melting. This spread is not easily interpreted as to the amount of cis  $\text{TC1}_2$  this introduces into the reaction at time zero, and might account for the low melting product isolated. There did not appear to be a significant difference between the amount of cis material isolated when comparing once and twice recrystallized starting materials.

Taking a combination of the possibilities suggested above, a reaction mechanism is proposed which incorporates them.



This proposed mechanism is in accordance with the views presented in reference 16 on page 370, that greater aromaticity is obtained from the phosphorous d orbital when polarized by electron withdrawing groups, thus the phosphorous is going to be in a more stable configuration when it is positively polarized as shown. The high entropy term is then reasonable, if one considers the obvious steric interference of the transition configuration with the added loss in entropy due to tying up an additional solvent molecule. This configuration would also be expected to reduce to some extent any motion that the tetramer normally undergoes when in solution, such as shifting between a boat and chair configuration, generally attributed to the tetramers. This mechanism further would not require a high enthalpy of activation since delocalization is not lost and the strength of an oxygen to phosphorous bond is approximately equal to the chloride to phosphorous bond.

The second substitution should be similar in nature to the first substitution. The data from the analog computer does not support this. Since the system is quite complex during the second substitution, the values for activation should generally be studied with a more refined

## B. GAS PRESSURE STUDIES

The fact that there is considerable uncertainty in the values reported from these studies is understandable, based on the approximations used in establishing the reaction parameters. A major approximation which is known to have introduced error was that the volume of melt liquid was the same for each run. The value chosen of twenty ml is considered accurate only to plus or minus one-half of a milliliter. In addition, there is the error associated with the p-hydroxybiphenyl which sublimed to the level of the hot oil in each run. A small error was introduced in the calculations because the volume of 136 ml of the gas system is considered accurate to plus or minus one-half a cubic centimeter. Another error is the one introduced by the temperature gradient which must exist in the reaction vessel since the oil temperature was 180°C above the ambient temperature of the major portion of the vacuum system.

These variances do not prevent some discussion on the values of activation obtained using the reaction rates obtained on the analog computer. The Entropy of activation of  $-42.5 \pm 10.0$  cal per mole degrees K is high. However, even the lower value of -32.5 suggests that much steric hindrance must be overcome in the transition state. It further suggests that additional ordering is taking place, which could be attributed to either solvent ordering or loss of freedom by the tetramer during the transition state. The relatively low value of Enthalpy of activation of  $13.6 \pm 10.0$  would indicate that if there is any ring delocalization, it is not lost during the transition state.

system than that used here, and it is not suprising that the data does not support the view that both reactions should operate through the same mechanism. But in defense of why the two reactions should follow the same route, it can be said that the biphenyl oxide should be just as efficient at polarizing the phosphorous as the chloride, and by the time any difference is transmitted around the ring to the second reaction site, it should have no effect on the next reaction.

There still remains the question of the existence of the proposed intermediate. The failure to isolate it does leave doubt as to its existence. The most logical place to have found the intermediate would have been in the material which was treated by sublimation during the KOH absorber isolation steps. The elemental analysis and the ir data of the material remaining after the removal of the p-hydroxybiphenyl show a probable mixture of high and low melting product. The chloride content suggests the presence of a small amount of either  $\text{TC1}_2$  or the proposed intermediate. If, in fact, there was some  $\text{TC1}_2$  or intermediate present, the sublimation conditions could easily destroy them. That is, with a temperature of  $130^\circ\text{C}$  and a continuous withdrawal of gas, a potential exists to drive the intermediate and/or  $\text{TC1}_2$  to product.

## VI. CONCLUSION

The reaction of substituting an alcohol for chloride on the tetramer of phosphonitrile is extremely fast at temperatures in the range of 200°C. The speed at which this reaction takes place at this temperature precludes the formation of long chain polymers due to the fact that too many initiations take place, thereby using up available reaction sites before satisfactory chain lengths have been reached. The only hope for long chain polymerization is in poisoning the reaction melt or by locating a satisfactory solvent for lower temperature work.

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13. ABSTRACT <p>In this research, a study of the kinetics and mechanism of the biphenyloxide substitution for chloride on the hexaphenyldichlorotetraphosphonitrile molecule was conducted. The reaction was studied in sealed, evacuated ampoules at 210 °C and in an evacuated gas pressure measuring system at temperatures of 185°C and 195°C.</p> <p>Two isomers of the expected disubstituted product were isolated by fractional recrystallization from acetonitrile. The isomers had melting points of 204°C and 174°C.</p> <p>The gas pressure studies provided extent of reaction versus time curves. An analog computer was used to simulate the reaction and the rates obtained were used to determine the <u>Entropy of activation</u> as <math>-42.5 \pm 10.0 \text{ cal mole}^{-1} \text{ degree K}^{-1}</math> and <u>Enthalpy of activation</u> as <math>13.6 \pm 10.0 \text{ Kcal mole}^{-1}</math> for the first substitution.</p> <p>A mechanism consistent with these values is proposed and discussed.</p>
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## KEY WORDS

## LINK A

## LINK B

## LINK C

ROLE

WT

ROLE

WT

ROLE

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Hexaphenyldichlorotetraphosphonitrile

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